Five-year Strategic Plan

BROOKHAVEN
NATIONAL LABORATORY

Center for Functional
Nanomaterials

March 2019

Table of Contents

1. EXECUTIVE SUMMARY

The Center for Functional Nanomaterials (CFN) is a Nanoscale Science Research Center operated for the U.S. Department of Energy (DOE) at Brookhaven National Laboratory (BNL). As a national scientific user facility, the CFN offers users a supported research experience with top-caliber scientists and access to state-of-the-art instrumentation. The CFN mission is advancing nanoscience to impact society, by being an essential resource for the worldwide scientific community and by carrying out transformative nanoscience research to support the energy, economic, and national security of the United States. Deep strategic partnerships are crucial to CFN mission success, including the strong synergy with the National Synchrotron Light Source II (NSLS-II), also located at BNL.

The CFN Five-year Strategic Plan is implemented to most effectively serve a nanoscience community with evolving interests and needs, providing flexibility and nimbleness for taking advantage of new opportunities for impactful science. Three nanoscience Themes form the foundation of the Plan. They guide development of new, state-of-the-art facilities, reflect the technical expertise of the staff, and determine a unique CFN identity.

The subject of Theme One is *Nanomaterial Synthesis by Assembly*, which has an ultimate goal of realizing a design strategy for synthesis of materials with targeted functionally by assembly of nanoscale components into precise architectures. CFN research on self-assembly focuses on devising new strategies for interaction- and process-controlled assembly of components, discovery of the governing principles underlying self-assembly, and understanding assembly pathways using advanced *ex-situ* and *in-situ* characterization and computational methods. The recognized expertise of CFN scientists in self-organization of nanomaterials with soft matter molecules (*e.g.*, DNA and polymers) is crucial for developing novel approaches for self-assembling arrays and clusters based on molecular recognition, and for devising new ways of probing assembly phenomena *in-situ*, in real time, and at multiple spatial and temporal scales.

Efforts are focused on developing nanomaterial synthesis-by-assembly methods and realizing functional material designs from polymer, nanoparticle, biomolecule-based, and 2D material components. Automation of the synthesis-by-assembly process will provide parallelism and reproducibility, facilitate assembly of increasingly complex architectures, provide control of assembly pathways, and allow incorporation of real-time feedback during processing. Advanced characterization and new methods to probe structure include nanoscale coherent X-ray beams at NSLS-II and 3D imaging of nanostructures by cryo- and in-liquid electron microscopy. Theory and simulation complement the experimental effort, including developing effective self-assembly strategies, assessing of the inherent stability of resulting morphologies, and mapping the advantages and limitations imposed by kinetics.

The focus of Theme Two is *Accelerated Nanomaterial Discovery*. While historically the discovery and development of new materials has followed an iterative process of synthesis, measurement, and modeling, suitable integration of advanced characterization, robotics, and machine-learning provides an opportunity for radically accelerating the material design process. The CFN has a demonstrated record of discovering nanomaterials by applying new materials synthesis strategies, advanced characterization, and machine-learning. Integrating these efforts will enable autonomous platforms for iteratively exploring materials parameter spaces, which have potential to revolutionize materials science by uncovering fundamental links between synthetic pathways, material structure, and functional properties.

During the next five years, CFN scientists will conduct research and develop instruments toward accelerating the materials discovery loop. Realizing this vision requires advancing and automating all aspects of the discovery process, including: implementing combinatorial libraries and real time synthesis platforms; improving multi-modal characterization and analysis of complex datasets; and using machine-learning to drive experiments.

Theme Three emphasizes the study of *Nanomaterials in Operando Conditions*. Interrogating materials at the nanoscale to derive atomic-level information on physicochemical processes under operating conditions remains a forefront and evolving nanoscience research field. The CFN continues to augment its comprehensive suite of instruments for *operando* studies of nanomaterials such as catalysts, photocatalysts, and battery electrodes. In the next five years, the CFN will increasingly integrate its *operando* capabilities together and with complementary ones being developed at NSLS-II to strengthen BNL leadership in multimodal *operando* nanomaterial studies.

CFN users, working independently or collaborating with CFN staff, use combinations of *in-situ* and *operando* capabilities at high temperatures and variable pressures to understand catalytic reaction mechanisms. Aberration-corrected transmission electron microscopy with high spatial and energy resolution illuminates reaction pathways and structural changes in energy storage systems. Scanned-probe microscopy, infrared reflection absorption spectroscopy, and X-ray photoemission spectroscopy provide details on the elementary reaction steps through coordinated studies of model catalyst systems. Computational methods link atomistic structures to specific spectroscopic signatures and with catalytic functionality.

The foundational Pillars for implementing this Strategic Plan are: an expert staff, an engaged user community, and a portfolio of strategic research partners — all working safely and supported by excellent operations and a portfolio of state-of-the-art nanoscience facilities. The CFN will strive for higher levels of user engagement, through strategic partnerships with larger initiatives with synergistic goals, technical workshops customized to communities with specialized needs, and by more visibly promoting user science accomplishments. During the next five years, the CFN will invest in new instrumentation and make major upgrades to its distinctive capabilities, and also develop new data-analytics and data-management methods to maintain its status as a cutting-edge Facility.

A high priority is continuing to enhance the partnership between CFN and NSLS-II, through investing further in four partner X-ray nanoscience instruments; working together to identify and capitalize on opportunities to create unique, new capabilities; and advancing joint projects with NSLS-II staff and users that exploit the complementary properties of X-rays and electrons to collect multimodal information on the same samples.

2. MISSION AND VISION

The Center for Functional Nanomaterials (CFN) is a state-of-the-art nanoscience facility with the dual mission of enabling the research of external users and carrying out transformative basic nanoscience research to discover, understand, and implement energy-related nanomaterials. The combined expertise of the scientific staff, portfolio of distinctive nanoscience capabilities, and strong partnership with the National Synchrotron Light Source (NSLS-II) at BNL, make the CFN unique among nanoscience centers worldwide.

The rapidly-changing scientific and technological landscape makes the CFN more central than ever to the US scientific community. The tightly integrated state-of-the-art nanoscience facilities and the deep scientific expertise of the staff allow CFN users to pursue complex projects involving nanomaterial synthesis/fabrication, advanced characterization, and understanding of nanomaterials all under one roof.

Having completed more than 10 years of successful operations, the CFN has become an open hub for nanoscience research, where engaged users and expert staff use the most advanced tools for breakthrough discoveries of new materials and phenomena that manifest at the nanoscale. An important element of CFN operations is forming deep research partnerships, for example by maximizing the value of co-location with NSLS-II and the complementarity of the two user facilities.

3. INTRODUCTION

In more than 10 years of nanoscience operations, the CFN has fostered continued growth of a large, productive community of users who benefit from both the state-of-the-art nanoscience facilities and the scientific expertise of CFN staff. The number of annual users has reached 581 (FY18), with users continuing to express high satisfaction with their CFN experience. The FY18 survey of user satisfaction indicated that 93% of respondents were either highly satisfied (86%) or satisfied (7%) with the service provided by CFN staff. The number of CFN publications was 305 in CY2018, with 25% appearing in high-impact journals, and almost 50% of them being the result of collaborations between users and staff.

While the CFN user community is both geographically and topically diverse, many user nanoscience projects cluster around themes addressing key scientific questions and technological challenges. These themes correlate naturally with the distinctive facilities and expertise of CFN scientists. As a result, the CFN has fostered a strong community of user and staff researchers working in pursuit of new scientific understanding in catalysis, energy conversion and storage, and nanomaterial self-assembly, among

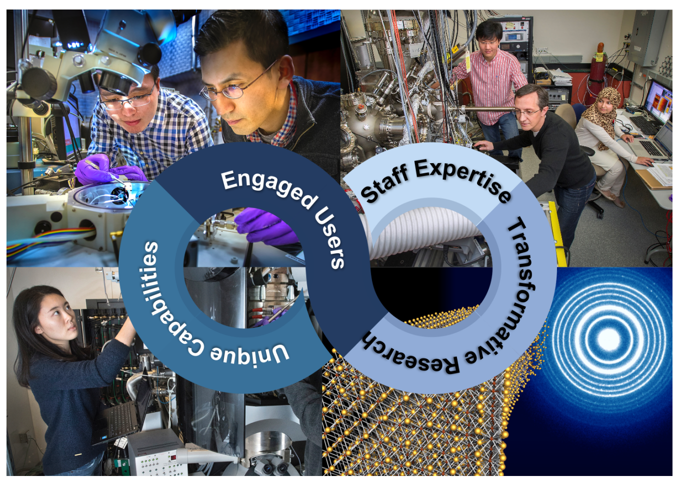

Figure 1. CFN users and expert staff work in collaboration or independently, taking advantage of unique capabilities to address complex scientific questions and technological challenges in nanoscience. The staff is recognized for its international leadership in electron microscopy, DNA-mediated and block copolymer nanomaterial self-assembly, among other areas. Advanced CFN capabilities in *operando* probes, aberration-corrected electron microscopes, and high-resolution lithography stand out.

other areas.

The CFN operates in a rapidly changing scientific world. New classes of materials have emerged, such as the expanding palette of new, ultrathin two-dimensional materials derived from layered Van der Waals solids. Heterostructures created from 2D building blocks can possess new types of electronic structure that hold promise for quantum information science. The demand to characterize materials in *operando* has grown, for example in efforts to bridge the gap between catalysts operating under industrial conditions and model catalysts probed under idealized conditions. Experiments and instruments are becoming increasingly complex, especially when measurements under variable conditions (*e.g.*, pressure and temperature) are added to those of static parameters. New ways of collecting information about the effects of those variables have led to an explosion of scientific data. CFN users utilize multiple facilities, including advanced characterization by electron and photon probes. The CFN conducts a focused program of internal research and continually develops new facilities and expertise to take advantage of opportunities. For example, the CFN continues to develop instrumentation in the strategic area of *operando* nanoscience probes. The CFN has successfully executed a comprehensive plan for developing and supporting a set of X-ray nanoscience capabilities in partnership with NSLS-II, deepening the strong partnership between facilities. As a result, the CFN is extremely well positioned to realize its vision and accelerate the DOE basic science mission.

This Strategic Plan is a guide to the drivers of CFN actions for the next five years. The Plan supports the dual CFN objectives of being an essential resource for users and producing transformative nanoscience breakthroughs. Progress on this Plan will be gauged periodically using criteria detailed in the Metrics section. Fully implementing the Plan requires prudently allocating Resources for upgrading facilities, installing new capabilities, and building and maintaining a world-class staff equipped with the appropriate technical skillsets.

4. OBJECTIVES AND THEMES

The objectives of the Strategic Plan follow directly from the two-fold CFN mission:

- The CFN will be an essential resource for the scientific community, enabling user projects that address fundamental questions and outstanding technical challenges in nanoscience.
- The CFN staff will conduct a program of internal research that produces transformative nanoscience breakthroughs.

Success relies on both the expertise of the CFN staff and the state-of-the-art nanoscience facilities they develop and operate. Naturally, staff and facilities support a broader range of user nanoscience projects than the narrower scope of the internal research program. However, many projects carried out by CFN users can be grouped into categories that strongly overlap topics underpinning the in-house research program, and which the CFN facilities are well-suited to address. This triple alignment is very positive, providing an efficient approach to complex, multi-disciplinary science and ultimately determining the CFN identity

The scientific questions underlying many CFN projects fall under three themes:

- Nanomaterial synthesis by assembly;
- Accelerated nanomaterial discovery; and
- Nanomaterials in *operando* conditions.

These themes utilize the leading expertise of CFN staff in nanomaterials synthesis, block copolymer self-assembly, and DNA-mediated nanostructures. They uniquely leverage the CFN capabilities for *in-situ* imaging and spectroscopy, and X-ray based techniques both at the CFN and at NSLS-II. The successful development of these three Themes rests on five sustaining Pillars, which are:

- Conducting research with Safety and Operational Excellence;
- Hiring and mentoring an Expert Staff;
- Fostering and supporting an Engaged User Community;
- Providing State-of-the-art Facilities for nanoscience; and
- Engaging in Partnerships for broadest impact.

Figure 2. The CFN Strategic Plan pursues the dual objective of making the CFN an essential resource for the nanoscience community and producing scientific breakthroughs in energy-related nanomaterials. Three overarching scientific Themes are supported by five Pillars.

4.1 Theme 1: Nanomaterial Synthesis by Assembly

The CFN is pursuing fundamental research into nanomaterial synthesis by assembly. This theme encompasses approaches based on self-assembly— which is a promising avenue to achieving high levels of nanomaterial complexity, those that use traditional and emerging thin-film processing methods such as nanofabrication and 3D printing, and still others that combine 'top-down' and 'bottom-up' methods.

Advances in chemical and biological synthesis methods have resulted in a wide palette of structurally-diverse and property-specific nanoscale components, including complex polymers, supramolecular complexes, designed proteins and DNA constructs, and sculptured nanoparticles. The availability of this material toolkit provides an opportunity for by-design assembly of components into complex, functional architectures with prescribed spatial organization and material composition. For example, materials with negative refractive index, and tandem catalyst materials, are each multi-component architectures having highly specific, nanoscale precision.

Longstanding CFN research on self-assembly focuses on new strategies for creating targeted nanomaterials *via* spontaneous assembly of components and discovering the governing principles underlying self-assembly. The program integrates experimental and computational efforts in order to understand, control, and design architectures through self-assembled systems, and to gain a mechanistic understanding of the underlying processes and assembly pathways using *in-situ* measurements. A long-term goal for CFN is developing a nanomaterial *inverse design* strategy, wherein assembly procedures for achieving specific structures/compositions are defined so as to permit true nanomaterial design for targeted functionally.

CFN staff are pursuing research in a broad range of self-assembling nanomaterials, including: nanoparticles, DNA systems, biomolecular constructs, polymers, zeolites, and 2D materials. Staff and users have used these components as material synthesis-by-assembly platforms. For examples, DNA assembly methods have been applied to create materials with either optical and chemical functions. Similarly, block copolymer assembly has been used to create antireflective optical coatings, and water-repellent surfaces.

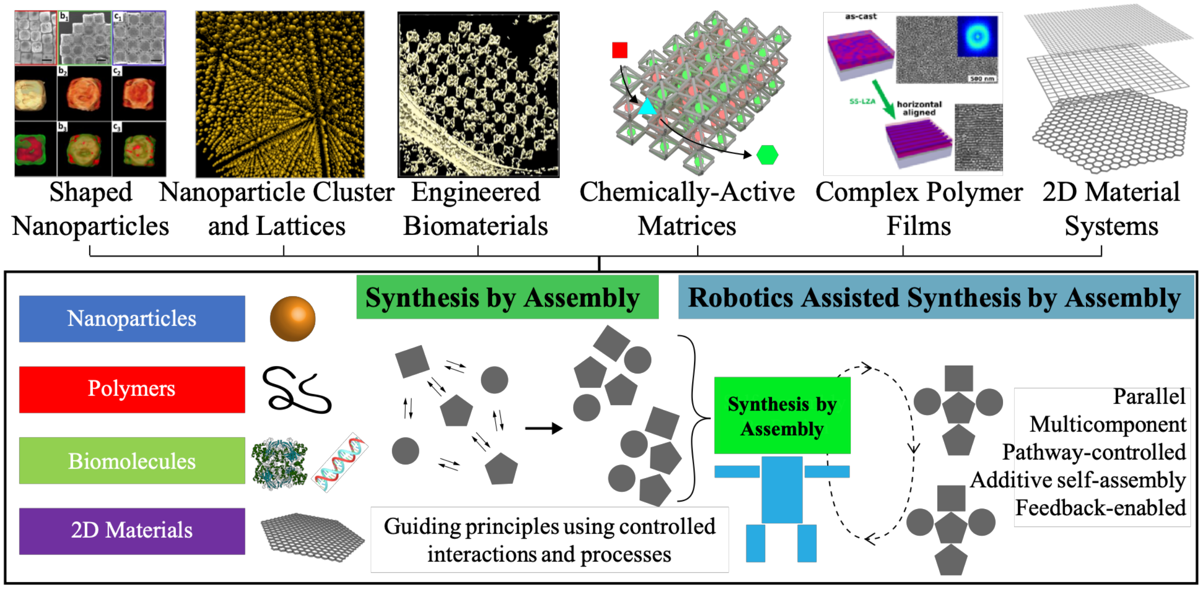

Figure 3. Nanomaterial Synthesis by Assembly is realized through discovery of guiding principles of self-assembly by design, and development of effective structure-formation processes. Robotic-assisted synthesis by assembly platforms will address challenging aspects of structure formation for creating a broad range of nanomaterials with targeted architectures and functions.

The CFN will advance the science of synthesis by assembly for design of targeted nanomaterial architectures by integrating self-assembly methods with robotic platforms (robot-assisted self-assembly). Automation of the synthesis-by-assembly process will provide parallelism and reproducibility, facilitate assembly increasingly complex architectures, provide control of assembly pathways, and allow incorporation of real-time feedback during processing.

This effort relies on cutting-edge characterization methods such as X-ray scattering, electron microscopy, single-molecule optical detection, and photon- and electron-based tomography — and will ultimately integrate *in-situ* characterization into the synthesis process for real-time structure/property monitoring and feedback. Current and planned X-ray characterization capabilities at NSLS-II will probe assembled nanoarchitectures across spatial and temporal scales and environmental conditions.

In the next five years, scientific efforts will be focused on development of nanomaterial synthesis-by-assembly methods and realizing functional material design from polymer, nanoparticle, biomolecule-based, and 2D material components. The ultimate goal is creating architectures with multiple levels of structural and compositional complexity, designed and built to achieve new optical, chemical, and mechanical functions. Major directions include:

- Nanoparticle periodic arrays with predefined organization and composition, to provide unique ways of controlling collective properties and deliver high-performance materials. Building on the new CFN directionally-functionalized nanoparticle platform will enable formation of lattices with target symmetry and multiscale internal particle organization. through synergetic connections of experimental, theoretical, and computational efforts.
- Expanding CFN expertise in self-assembly towards incorporating functional biomolecular complexes into nanostructured materials and gaining control over building structurally-prescribed biomaterial systems. Nanostructured biomaterials synthesized by assembly can

enhance biochemical reactions, promote interactions of biomolecules with inorganic, organic and biological matter, and provide new sensing modalities.

- Prescribed organization of nanoparticles into designed 3D cluster architectures with location control of different particle types within the structure. Design of nanoarchitectures for modulating optical, magnetic, and catalytic properties of nanoparticles through collective and proximity effects. These synthesis by assembly efforts will couple advanced structural and functional characterization.
- Pathway assembly control of self-assembled nanostructures on different length-scales. Using non-equilibrium behavior of systems, it will be possible to manipulate different length scales during material self-assembly. For example, CFN staff will using photo-thermal stimulation to achieve simultaneous patterning of block copolymer films at the microscale, with molecular-scale self-organization over wide areas.
- Developing methods for surface-grown nanoparticle lattices by merging block copolymer patterning with DNA-based nanoparticle assemblies. Establishing methods for morphological control of lattices, understanding growth mechanisms using *in-situ* surface scattering methods, and developing approaches for creation of commensurate and non-commensurate arrays using different surface patterns and DNA-linking motifs.
- Controlled fabrication of sculpted nanomaterials with atomically defined planes. Continued development of the CFN platform for shape-controlled nanoparticles will provide new materials with potential for impact in other research areas, such as catalysis and support both hybrid organic-inorganic self-assembly strategies and template assembly of inorganic materials as such.

To advance these scientific directions, major methods and capabilities will be developed:

- Robotic platform for automated synthesis-by-assembly of multicomponent systems with in-line characterization and feedback control, including nanoparticle-based materials, DNA organizations, and molecularly structured biomaterials.
- Automatic synthesis, separation, and purification of shape-controllable noble metal nanoparticles at large-scale and with high-fidelity.
- Time-correlated X-ray methods to probe dynamics of nanoparticle lattices and mass transport phenomena at nanoscale.
- X-ray and electron tomography methods for revealing structural and chemical 3D local organization of nanoscale assemblies using newly developed nanometer X-ray beams and electron microscopy approaches.
- Micro-beam synchrotron light scattering for multiscale phase mapping of nanostructured materials on a range of scales, from molecules to macroscopic dimensions.
- Cryo and in-liquid electron microscopy for imaging of 3D nanoparticle and protein arrays and clusters. New CFN developed electron microscopy methods for 3D imaging of soft-matter objects and their arrays with sub-nm accuracy, including DNA constructs, proteins and polymers.
- Extend single-molecule optical methods to probe local optical fields, energy transfer processes, polarization and material heterogeneity. Extend theory and simulation capabilities by developing effective force fields that physically describe the key characteristics of the designer interparticle interactions employed in CFN self-assembly strategies.

4.2 Theme 2: Accelerated Nanomaterial Discovery

Modern materials are increasingly complex. Formed from a wide range of components, they exhibit structural order at multiple length scales (atomic, molecular, nano, meso, micro, macro), are synthesized using elaborate processing pathways, and are frequently non-equilibrium. As well, the functional demands on new materials are increasing, as they are designed for performance improvements for next-generation applications (e.g. energy materials, materials for quantum information sciences, or enhancing optical or mechanical properties). Historically, new materials development has followed an iterative process of materials synthesis, measurement, and modeling. Tightening this discovery loop has potential for radically accelerating the design of new materials and revolutionizing materials science. Guided experimentation using data analytics and combinatorial sample libraries enables data-driven materials discovery. Autonomous platforms leveraging robotics, advanced characterization, and machine-learning can iteratively explore material parameter spaces and uncover fundamental links between synthetic pathways, material structure, and functional properties. Ultimately, real-time steering of material synthesis is envisioned.

This theme builds from core CFN strengths in synthesis, characterization, and theory/analytics, which have contributed discovery of materials with novel properties. For example, synthesis of hybrid polymer/inorganic materials *via* infiltration of organometallic precursors is an method for continuously tuning material composition, electrical, and mechanical properties. Ultrafast optical characterization has been used to make the first discoveries of intramolecular multi-exciton generation in organic molecules, demonstrating that new material discovery can occur through functional characterization. The CFN has demonstrated an approach to extracting local atomic motifs from X-ray scattering spectra, by applying machine-learning to scientific datasets.

During the next five years, CFN scientists will conduct fundamental research to further accelerate the materials discovery loop. Realizing this vision requires advancements and automation of all stages of materials discovery: materials synthesis, especially by implementing combinatorial libraries and real time synthesis platforms; characterization, including multi-

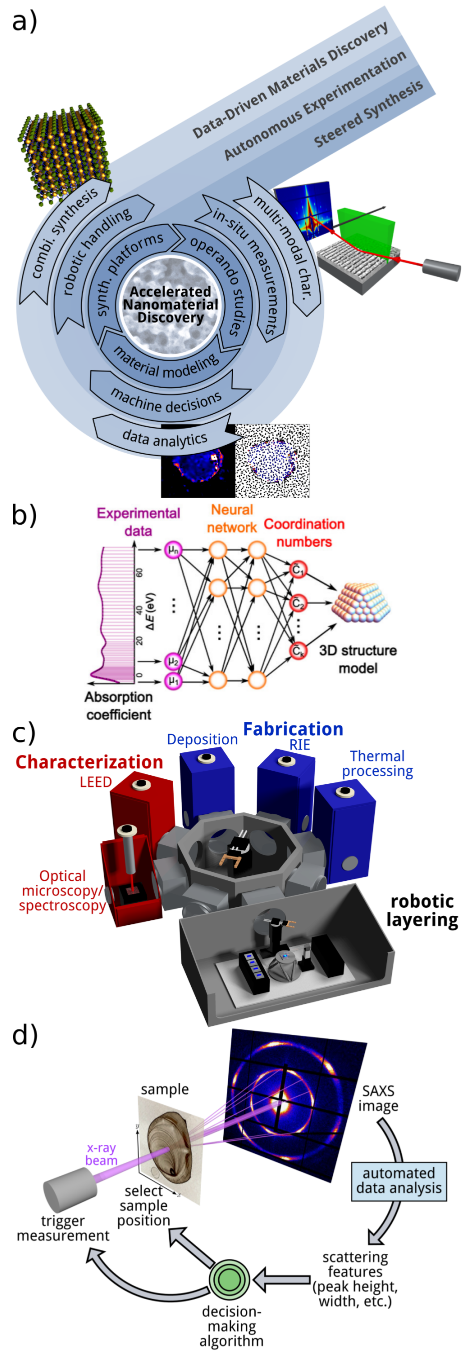

Figure 4. Accelerated Nanomaterial Discovery. (a) The discovery loop can be tightened by close coupling of automated synthesis, measurement, and analytics. (b) Machine-learning has been used to convert from X-ray spectra to local structural motifs. (c) The QPress will be an automated platform for constructing 2D material heterostructures by assembly. (d) Autonomous experiments have been implemented at a synchrotron X-ray scattering beamline.

modal *in-situ*/*operando* measurements; and understanding through theory/analytics and use of machine-learning to drive experiments. CFN efforts will be guided by key questions that currently limit the implementations of automated discovery platforms, such as:

- *How can functional nanomaterials by synthesized parametrically*? The CFN will pursue combinatorial methods for synthesis of inorganic, soft, and hybrid nanomaterials. For example, electrospray deposition can generate in-plane and out-of-plane gradients in material compositions and thickness. The CFN will advance synthesis methodologies for desired functionalities, especially in hybrid and hierarchical nanomaterials. A primary target will be developing platforms that provide *in-situ* property measurement during synthesis.
- *How can the materials discovery loop be more efficient*? The CFN will continue to advance its expertise in advanced nanomaterial characterization, especially *in-situ* and *operando* probes, with the goal real-time studies during synthesis and processing. These characterization methods will be integrated with data analytics and decision-making algorithms/software to enable machine-guided experimentation.
- *How can theory/data analytics uncover fundamental materials physics*? The CFN will advance the modeling of materials by improving existing theories and coupling these to modern machine-learning methods. These methods will be used to data-mine expanding datasets, to search for previously ignored trends in materials behavior and universalities that underlie materials synthesis. For example, the behavior of many disparate self-assembling material systems may be described by appropriate abstraction of inter-object forces.

These studies will provide improved materials knowledge and new, robust platforms for studies of nanomaterials during synthesis, assembly, and processing. These platforms will benefit broad nanomaterials communities by empowering a host of searches for novel materials. Some ongoing and targeted developments are:

- Developing improved algorithms for control of experimental platforms. We will develop machine-guidance algorithms that are applicable to a wide range of problems, and others that are closely-coupled to specific material classes.
- The Quantum Material Press (QPress) will be a cluster tool capable of automated exfoliation and characterization of 2D materials, and assembly of 2D components into stacked heterostructures with tailored quantum properties. This automated platform will enable fabrication of quantum devices with previously impossible complexity.
- A suite of combinatorial methods for synthesis and processing of inorganic, soft, and hybrid materials. This includes flow-coating for film thickness gradients, electrospray for composition gradients, photo-thermal annealing for processing gradients, solvent annealing, infiltration synthesis, gradient deposition of multi-phase materials, and 2D/3D lithographic sample arrays.
- Specialized X-ray spectroscopy studies, coupled to machine-learning models, for establishing spectral-structural assignments and uncovering local atomic motifs. This enables, for example, understanding of how structural motifs at interfaces influence catalytic activity, and to discern whether catalytic operation changes material structure.

4.3 Theme 3: Nanomaterials in *Operando* Conditions

Characterizing nanomaterials during operation in their native environments is vitally important to modern materials science. Interactions with highly reactive environments lead to dynamic changes in material physical and electronic structure, which may only be observable under functional conditions. Discovery of structure-function relationships hinges on *in-situ* material investigations.

For example, synthesis of new catalysts hinges on identifying active phases and reaction mechanisms, *as they emerge at the elevated pressures and temperatures under which catalysts operate*. Transmission electron microscopy (TEM) and local area electron energy loss spectroscopy (EELS), scanning tunneling microscopy (STM), low energy electron microscopy/X-ray photoemission microscopy (LEEM/XPEEM), infrared (IR) spectroscopy, and ambient-pressure photoemission spectroscopy (AP-PES) comprise a laboratory- and synchrotron-based toolset capable of *operando* nanomaterial interrogation. Atomic scale theory links key structural motifs to complex spectra and observed characteristics.

The CFN has assembled a comprehensive suite of tools for understanding materials as diverse as catalysts, photocatalysts, and battery electrodes. *In-situ* and *operando* implementations of these core techniques area a frontier area of research, as is their integration for multidimensional characterization. Time-resolved perturbations by modulation excitation spectroscopy (MES) can provide kinetic data, and the CFN will implement this technique into both AP-PES and IR spectroscopy, and innovate new methods for making use of the resulting complex datasets. In the next five years, the CFN will further advance its capabilities for *in-situ* and *operando* measurements and integrate them with others being developed at NSLS-II. A universal holder and vacuum suitcase will facilitate sample transfers for multimodal material studies. The CFN will develop accompanying methods in data analytics to extract and interpret the rich information derived from multidimensional datasets. The goal is strengthening BNL's position as a world leader for multidimensional *operando* studies of nanomaterials.

CFN users and staff are interested in catalysts for greenhouse gas-to-fuels and biomass conversion, with metals dispersed on nanoporous materials such as zeolites and metal organic frameworks, or integrated inside them. Chemistry in nanoconfined spaces can affect the formation of active centers and reaction pathways, and can change the required reaction conditions. Copper-based catalysts, for example, show promise for hydrogenation of CO_2 to methanol and direct conversion of methane into alcohols. Stabilization of active Cu ensembles in nanoporous materials with local effective high pressures can facilitate their detailed study under *operando* conditions.

A different type of reaction in which *in-situ* characterization is of great importance is photocatalytic water splitting. Photocatalysis requires separation of photoexcited charge carriers on ultrafast timescales, to avoid recombination losses. Ultrafast optical spectroscopy is uniquely suited to quantifying recombination losses and understanding how they can be suppressed through nanoscale material and interface design. Catalytic steps occur on longer time scales, and changes in the local structure of active centers can be understood using *operando* XAS, AP-PES, and IR measurements.

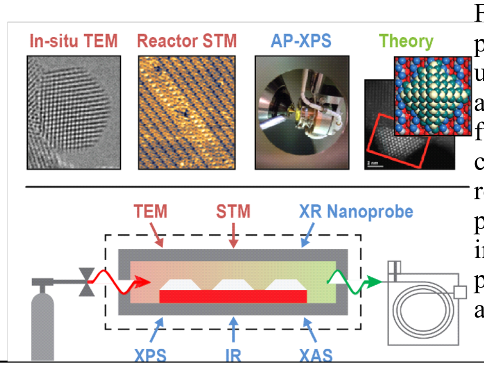

Figure 5. Nanomaterials in *Operando* Conditions. The CFN portfolio of *in-situ* and *operando* techniques using electrons, ultrafast photons, and X-ray radiation, coupled with theory, creates a unique setting for studying the link between structure and function of nanomaterials. A key element of this approach is correlating multimodal imaging and spectroscopy with real-time reactivity measurements. This can be done using portable high-pressure reaction cells in which the same materials are interrogated in *operando* by electron probes at the CFN and complementary photon probes at NSLS-II or using vacuum transfer of samples among ambient pressure systems and reactors.

A third area where it is crucial to probe materials in complex environments is energy storage. Creating electrochemical batteries with both high storage capacity and high cyclability requires understanding electrochemical processes at electrode/electrolyte interfaces, including structural and phase changes, electron/ion insertion mechanisms, and the dynamical evolution of the interface structure. CFN users studying Li-ion (and other alkali-ion) batteries are interested in resolving the reaction pathways and unlocking the potential of novel materials such as disordered layered oxides as battery electrodes. The combination of synchrotron-based techniques with electron microscopy provides critical insights into these processes.

In the next five years, CFN scientists and users will exploit this wealth of capabilities and expertise to understand nanomaterials under *operando* conditions, working on:

- Elucidation of catalytic reactions using a multimodal approach combining Reactor STM, AP-PES, IR, and *in-situ* TEM, all operating at elevated local pressure and temperature;
- Optimization of separation of photogenerated charged carriers at nanostructured hybrid organometallic/oxide interfaces of photocatalysts using *in-situ* ultrafast optical spectroscopy and light-modulation excitation spectroscopy and X-ray spectroscopy, including *operando* XAS at NSLS-II;
- Investigations of reaction pathways in the electrode structure of energy storage systems using TEM-based methods with high spatial and energy resolution.

A unique CFN strength derives from multimodal integration of complementary methods to probe the *operando* behavior of nanostructured functional materials, and will be further enhanced by major instrument and method development, namely:

- The CFN will develop a unique environmental, monochromated, aberration-corrected scanning transmission electron microscope (E-STEM) designed for high-resolution studies of structural and chemical evolution of nanomaterials in working environments;
- Upgrades to existing AP-PES instruments will provide multimodal *operando* spectroscopy capabilities for interrogating gas/solid interfaces. Use of tender X-rays combined with new liquid cells provide an ability to characterize liquid/solid interfaces, including during nanomaterial synthesis and electrochemical processes;
- Developments at lab-based AP-PES and AFM/IR spectroscopy instruments will guide upgrades at existing and new capabilities at NSLS-II;
- A suite of portable gas/liquid reactor cells will make it possible to interrogate the same catalyst or battery material under identical environmental conditions by TEM, AP-PES, and other X-ray spectroscopies at NSLS-II beamlines. These cells will measure gas pressure, reactant/product composition, temperature, and pH. Holders will be standardized across the portfolio of surface science instruments for sample transfer in vacuum among CFN and NSLS-II facilities, glove boxes, and synthesis facilities;
- Computational methods, including improved first-principles approaches and machine learning, will link atomistic structures to spectroscopic signatures obtained from simulated materials or structures on databases, and to unravel catalytic reaction pathways and networks from data obtained under reaction conditions.

5. PILLARS

Achieving the Objectives of this Strategic Plan requires an expert staff, an engaged user community, and a set of strategic research partnerships. World-leading research by staff and users must be conducted safely and supported by both excellent operations and state-of-the-art facilities

— including those developed and offered in partnership with NSLS-II. Implementing this Plan requires accompanying plans for strengthening these essential pillars, as detailed here.

5.1 Safety and Operational Excellence

Excellence in operations and a strong safety culture are central to the success of the CFN. The CFN emphasizes the importance of communication among the staff and diverse population of users. Research at the CFN is supported by a robust physical and administrative infrastructure. Effective management of the user experience from concept to project completion is key for productivity and user satisfaction. The CFN is dedicated to providing users and staff with a research environment in which safety is fully integrated into all aspects of the work. Regularly reviewed and updated course-based modules and on-the-job training play an essential role in safe and productive research. Prior to independent use of CFN facilities, every new researcher is introduced to safety and operations personnel and engages with an expert mentor for guidance on operation, hazard identification, and response. Specific focus areas include:

- Optimizing the facility development process to reduce and control hazards associated with facility usage and operations in general;
- Implementing a “cradle to grave” materials safety concept, placing equally-high emphasis on nanomaterials and chemical safety from project inception, through project execution, to final material disposal;
- Integrating web-based modules designed for efficient user and staff training, into a robust system to ensure that requirements are met prior to granting access to CFN facilities;
- Developing videos, operator aids, and Standard Operating Procedures to assist staff and users in safely carrying out infrequent or especially hazardous operations.

5.2 Expert Staff

In order to be a preeminent research facility, the CFN pays special attention to recruiting, developing, and retaining the highest-quality scientific, technical, and administrative personnel, following a strategy that includes:

- Seeking and recruiting a diverse workforce of the most talented professionals at all levels;
- Offering professional growth opportunities for staff that benefit their careers and the CFN. In this spirit, the CFN requires scientific staff to maintain an equal balance of effort (50/50) between support for CFN users and conducting internal CFN research;
- Maintaining vibrant post-doctoral researcher and Ph.D. student programs, which increase the scope and impact of the CFN internal research program, and provide opportunities to develop supervisory and mentoring skills;
- Fostering an environment in which scientific staff augment their research by capitalizing on opportunities external to the CFN, while maintaining their commitment to the user program. Examples include: BNL Laboratory Directed Research and Development program, DOE Early Career Awards, DOE Energy Frontier Research Centers, Small Business Innovation Research Programs, and partnering with CFN users in DOE initiatives, among others;
- Offering mentoring and professional development programs for all staff levels, in coordination with BNL Human Resources;
- Seeking recognition, internal and external to BNL, for professional achievements.

5.3 Engaged User Community

To fulfill its mission of serving a satisfied and productive external user community, the CFN continuously engages past and current users and actively seeks communities of new users. Also crucial is that users participate in the CFN culture and planning, well beyond facility usage and staff collaborations. The CFN is committed to achieving higher levels of user engagement with users, through initiatives that include:

- An Engaged Users' Executive Committee (UEC). The CFN UEC provides an organized framework for communicating user needs to CFN and BNL management. The UEC promotes and encourages effective use of the CFN by providing forums for organized discussions among users. Together with the NSLS-II UEC, the UEC organizes the annual Users' Meeting, with assistance from the CFN. The CFN will continue to actively engage the UEC for input on planned, future facility directions.
- Strategic Partnerships. CFN staff will strive to engage with user teams when there is a clear alignment of scientific interests, *e.g.*, specific Energy Research Frontier Centers.
- Enhanced Online Experience: The CFN is committed to optimizing the entirety of the user experience, from proposal submission, throughout data collection, and to the dissemination of research findings. The CFN will seek to streamline these processes, integrating systems for proposal review/allocation with scheduling, and implementing a system for coordinated user access to all BNL user facilities.
- Promoting User Science. The CFN will increase the visibility of user science by promoting their accomplishments within the CFN facility, online and through social media, and at scientific meetings and conferences.
- Technical Workshops. Experience shows that instrument/technique training and user development workshops are excellent ways of linking CFN staff and experienced users with targeted potential users over topics of shared interest. These events, plus complementary tutorials, serve as an effective outreach instrument to expand the community and will help solidify the identity of the user community.
- Reaching New CFN Users. The CFN will continue to strive to expand the geographical diversity of users by increasingly deploying staff as ambassadors at meetings and conferences. An element of this strategy is leading and participating in joint NSRC outreach events at national meetings.

5.4 State-of-the-art Facilities

The CFN facility is envisioned with the entire process of materials research in mind (synthesis and fabrication, advanced characterization, and understanding), such that CFN users access an integrated set of tools for a complete research experience under one roof. The CFN operates the most advanced instrumentation in nanolithography, materials preparation, and electron and photon probes, including those located at NSLS-II, and computational resources with diverse software tools for nanoscience theory, simulation, and data analytics.

The CFN portfolio of instrumentation is strategically refreshed to provide cutting-edge facilities, internationally attractive to high-impact users. The CFN will continue its sustained initiative to develop and operate new, unique nanoscience tools in partnership with NSLS-II. We will upgrade existing major CFN capabilities and acquire key new instruments. The Plan envisions investments driven by the needs and trends in materials research demand. Specifically:

- A new CFN, lab-based AP-PES instrument has been installed to complement the AP-XPS capability at the IOS beamline at NSLS-II for studies of materials such as nanocatalysts *in-*

situ under ambient pressure of target gases. Use of this lab-based instrument will serve a broad array of user needs, including preparatory experiments that will enable more efficient use of limited beam-time on the NSLS-II based instrument. It will be the platform for CFN development of new capabilities such as liquid cell environments, atmospheric pressure flow reactors and concentration modulation excitation spectroscopy.

- The CFN now operates its aberration-corrected low-energy electron microscope / photoemission electron microscope (AC-LEEM/XPEEM) at the Electron Spectro-Microscopy (ESM) beamline at NSLS-II. This instrument delivers dramatically improved spatial resolution (< 2 nm) and nearly tenfold higher transmission, relative to non-corrected systems at other user facilities around the world. Planned upgrades include capabilities for cryogenic operation of the instrument and a new a new analyzer to deliver world record XPEEM energy resolution.
- The CFN continues to invest in its partner X-ray scattering endstations at NSLS-II: the Complex Materials Scattering (CMS) and Soft Matter Interfaces (SMI) beamlines. Analytics software at SMI will be enhanced to take full advantage of the CFN provided large-q-range detector. Modes of high-throughput and autonomous experimentation at CMS will be further developed by integrating novel real-time materials processing platforms, including photothermal thin film processing and automated liquid handling.
- The CFN has participated in a proposed infrared spectroscopy (IR) beamline at NSLS-II (INF) that will include three simultaneously operating branches: (1) an infrared near field nanoscopy instrument (INFN) dedicated to condensed matter physics; (2) a second INFN instrument installed by the CFN and set up to carry out first of its kind experiments in controlled environments from UHV to ambient conditions; and (3) direct synchrotron IR light to combine photoelastic modulation infrared reflection absorption spectroscopy (PM-IRRAS) with AP-PES at the CFN-partner endstation IOS. The system will be set up to carry out INFN experiments in controlled environments, a capability that currently does not exist anywhere in the world by building on developments from our recently installed lab-based nano IR system.
- Reactor cells and universal sample holders for vacuum suitcase transfer that enable *operando* experiments have been demonstrated for multi-modal experimentation, including probes by X-ray absorption, infrared spectroscopy, and transmission electron microscopy. Use of these cells and holders is expanding, including in the FEI Titan ETEM and FEI Talos TEM/STEM instruments. New machine-learning-based data analysis approaches are being developed to link spectra and images to structural motifs.
- The CFN is building a revolutionary cluster tool that will automate the handling of two-dimensional materials, as well as the synthesis of layered heterostructures from such materials. The overall system will feature robotic exfoliation from van der Waals crystals, automated characterization (microscopy and spectroscopy) and processing (thermal, plasma), machine-guided materials layering, and machine-learning software to streamline data analytics.
- The CFN is developing a suite of thin film formation and processing tools that will enable the creation of combinatorial sample libraries in soft and hybrid materials. Tools include flow-coater to generate thickness gradients, electrospray to create in-plane and out-of-plane composition gradients, as well as photothermal and solvent annealing stations for controlled processing.

The CFN partnership with NSLS-II

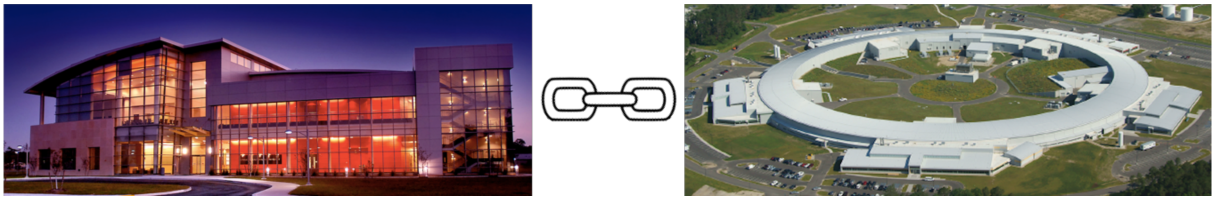

Figure 6. A strong partnership with NSLS-II is a key element of the CFN Strategic Plan. Three illustrative are:

Theme 1: Nanomaterial Synthesis by Assembly

The CFN has world-leadership position in DNA programmable self-assembly of heterogeneous nanomaterial lattices. CFN is developing methods using the advanced beamlines at NSLS-II to study how self-assembly can be used to organize targeted nano-components, especially optically and chemically-active species, into well-defined functional lattices.

Theme 2: Accelerated Nanomaterial Discovery

CFN has building an autonomous X-ray scattering endstation. Machine-learning methods have been created to automatically analyze X-ray scattering data. Algorithms for autonomous experiment control have been developed in collaboration with the DOE CAMERA project. In partnership with NSLS-II, these concepts have been implemented at a synchrotron scattering beamline for autonomous exploration of materials parameter spaces.

Theme 3: Nanomaterials in *Operando* Conditions

CFN has built an ambient pressure photoelectron spectroscopy (AP-PES) endstation. The endstation, one of the first to become operational at NSLS-II, has been installed and operated in partnership with NSLS-II. Combining information from *operando* experiments at the AP-PES endstation and the environmental transmission electron microscope (E-TEM) at the CFN, critical information from dynamic processes in catalysts can be interrogated, such as the catalytic growth of carbon nanotubes and fuel synthesis and conversion.

- We will further develop new capabilities to achieve spectrally, spatially, temporally, and polarization-resolved optical signatures on the single-molecule level. We will expand these characterizations to cryogenic temperatures and field-controlled environments to investigate structure, charge, energy transfer, and quantum effects in nanomaterials.
- Innovative software and data management, including use of machine-learning tools, as well as development and applications of physical theory, will be supported by regular CFN investments in new high-performance and high-throughput computing capabilities, data storage and communications in cooperation with the BNL Scientific Data and Computational Center (SDCC). CFN will support a range of access options to meet user needs, ranging from batch computing to web-based tools.

5.5 Partnerships

Leveraging its culture of collaboration and innovation, the CFN will develop and strengthen strategic research partnerships to maximize the impact of CFN expertise and capabilities.

Since inception, a key CFN facility strength has been the partnership with synchrotron light sources co-located at BNL. The CFN will continue to deepen its relationship with NSLS-II through investments in X-ray nanoscience instrumentation, joint projects, development of staff expertise, and streamlined access mechanisms. This relationship between facilities has benefitted users, who in many cases request coordinated access to both CFN and NSLS-II. Some examples include:

- The CFN has participated in developing new X-ray beamlines for nanoscience and maintains Partner User Agreements with NSLS-II to operate user programs at four endstations. Taking advantage of the brightness, coherence, and focusing at NSLS-II, these joint ventures are establishing leading capabilities in X-ray scattering, photoelectron spectromicroscopy, and *operando* spectroscopy. CFN is contributing essential equipment and staff, helping nanoscience users to access unique experimental capabilities.
- The CFN plans continued investments in these partnerships through major equipment upgrades and will explore new partnerships in areas of mutual scientific and technical interest, for example in hard X-ray spectroscopy and infrared spectromicroscopy.
- CFN capabilities and expertise are instrumental in developing new capabilities at NSLS-II. For example, CFN nanofabrication is used to create high-performance X-ray optics and reference samples for method development at beamlines.
- The CFN will continue to establish joint projects with NSLS-II staff and Users. For example, it will exploit the complementary properties of X-rays and electrons to image the same catalyst under realistic operating conditions, to interrogate working photo-electrochemical systems, and for the imaging and spectroscopic probing of soft and hybrid hierarchical systems.
- The CFN and NSLS-II are collaborating to develop and implement data analysis and machine learning software for large data sets collected in synchrotron-based and electron-microscopy experiments. This work benefits from the on-going BNL investments in its Computational Sciences Initiative. CFN has initiated pilot projects at several beamlines to develop advanced analysis methods.

The CFN will continue to establish partnerships with universities and industry in areas of strategic research overlap, to maximize the impact of CFN capabilities. Examples include strong engagements with Energy Frontier Research Centers in catalysis and energy storage, and emerging partnership opportunities in quantum information science. Intellectual property and technology transfer offer other ways to increase CFN impact. For example, CFN has recently transferred its nanostructured antireflection technology to a start-up company for commercialization. Finally, Partner users can provide investments of expertise and equipment that can help CFN grow in new directions.

6. METRICS & RESOURCES

6.1 Metrics

The ultimate measure of the success of this Strategic Plan is the extent to which the CFN is a community of users and staff renowned for nanoscience breakthroughs and societal impact. Each year, the CFN reports its progress to DOE and receives feedback through the DOE Performance Evaluation and Measurement Plan (PEMP). Every three years the CFN undergoes an onsite review by DOE, in which external reviewers assess the impact of internal and user science, as well as user satisfaction. The CFN management team, supported by the external CFN Science Advisory Committee (SAC), will regularly assess progress in executing the Strategic Plan. Progress will be measured along three lines focused on critical aspects of the CFN mission:

- Developing unique capabilities for the user community
  - Have the new capabilities been fully available to CFN users, and have users taken advantage of those capabilities?
  - Have those new capabilities led to impactful investigations not previously possible?

- How satisfied are the users with the effectiveness of the facilities and with the support provided by CFN staff?

- Fostering the success of world-class scientific staff
  - Has the CFN internal research effort resulted in scientific breakthroughs, published in top journals and widely cited?
  - Has execution of the research plan generated new intellectual property?
  - Are CFN staff members in leadership positions within their respective fields, with recognition for their accomplishments by the external technical community?
- Being an essential resource for collaborative research
  - Is the CFN engaged in multidisciplinary research partnerships involving academia, other national laboratories, and industry?
  - Is the CFN considered an essential resource in large-scale scientific efforts in catalysis, energy storage, or quantum information science?
  - Are CFN scientists key elements of collaborative teams in their areas of expertise?

6.2 Resources

Guided by user feedback, input from the UEC, and advice from the SAC, the CFN allocates resources (equipment, staff, and operating funds) to support each facility and ensure that high-impact research is carried out in each thematic area. CFN operations are primarily funded by a block grant from the DOE Office of Science. From this operating budget, the CFN invests +10% each year in new scientific equipment, and additional money as contingency for facility upgrades. Within the constraints of realistic future budgets, the CFN anticipates being able to successful carry out this Strategic Plan over the five-year period projected here.

However, to fully exploit the capabilities that will be developed in the scope of this Strategic Plan, several staff members will need to be added, spanning expertise that includes materials by design, coherent scattering, electron-microscopy analysis and simulation, and advanced methods for large-data analysis, visualization and machine learning. Additional funding, beyond conservative budget projections, will significantly enhance unique CFN capabilities.

If resources are more limited in the future, the CFN will adjust the scope of this Plan accordingly. In such a scenario, the CFN will establish priorities based on progress among the scientific themes, growth of high-impact facility usage, and input from the SAC and the user community, to ensure that the CFN fulfills its core mission and continues to thrive.